(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 1 063 396 A2

(12) **EUROPEAN PATENT APPLICATION**

(43) Date of publication:
27.12.2000 Bulletin 2000/52

(51) Int. Cl.[7]: **F01N 3/28**

(21) Application number: **00305225.5**

(22) Date of filing: **20.06.2000**

(84) Designated Contracting States:
AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU MC NL PT SE
Designated Extension States:
AL LT LV MK RO SI

(30) Priority: **22.06.1999 JP 17506999**

(71) Applicant: **NGK INSULATORS, LTD.**
Nagoya-City, Aichi Prefecture 467-8530 (JP)

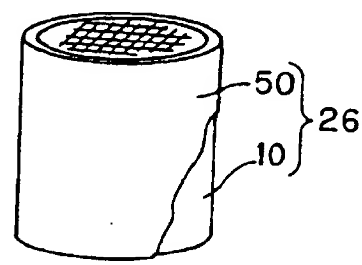
(72) Inventor:
Hijikata, Toshihiko,
NGK Insulators, Ltd.
Nagoya-city, Aichi-Pref. 467-8530 (JP)

(74) Representative:
Paget, Hugh Charles Edward et al
MEWBURN ELLIS
York House
23 Kingsway
London WC2B 6HP (GB)

(54) **Ceramic honeycomb structure, ceramic honeycomb catalyst carrier, and ceramic honeycomb catalytic converter using the same**

(57) A material having a thermal expansion co-efficient approximately the same as that of a catalyst is adhered to the entire outer side of an outer wall of a ceramic honeycomb structure or a ceramic honeycomb catalyst carrier, thereby providing a ceramic honeycomb structure, ceramic honeycomb catalyst carrier, and ceramic honeycomb catalytic converter using these. These structure, catalyst carrier, and catalytic converter are capable of preventing cracks at the perimeter of the ceramic honeycomb catalyst carrier, and hence capable of preventing damage to the ceramic honeycomb catalyst carrier in a sure manner.

FIG. 1(A)



Description

BACKGROUND OF THE INVENTION

1. Field of the Invention

[0001] The present invention relates to a catalytic converter which is a device for purifying harmful combustion gasses exhausted from internal combustion engines and the like, and more particularly relates to a ceramic honeycomb structure, a ceramic honeycomb catalyst carrier, and a ceramic honeycomb catalytic converter using these.

2. Description of Related Art

[0002] Currently, ceramic honeycomb catalytic converters are widely used as automobile exhaust gas purifying devices (See Fig. 3). Environmental issues in recent years along with even stricter exhaust gas restrictions are requiring that catalysts be able to function immediately following starting the engine when the exhaust gas is still cool, i.e., cold starts.

[0003] Accordingly, a step being taken is to reduce the thickness of the partitions of the catalyst carrier (ceramic honeycomb catalyst carrier) to 1/2 to 1/6 of the conventional thickness, so as to lower the thermal capacity of the catalyst carrier and speed up the temperature rising of the catalyst carrier, along with preventing deterioration of engine performance due to pressure loss.

[0004] However, with the above catalyst carrier, the thermal expansion difference between the inner side of the outer wall which carries the catalyst, and the outer side of the outer wall which does not carry the catalyst becomes great, so cracks easily occur at the perimeter of the catalyst carrier due to the hot exhaust gasses in actual use, and further, in the event that thermal and mechanical usage conditions are severe, the cracks at the perimeter of the catalyst carrier have been known to progress to the interior of the catalyst carrier, resulting in damage to the catalyst carrier or loss of catalyst functions.

SUMMARY OF THE INVENTION

[0005] The present invention has been made in light of the above-described current state, and accordingly, it is an object thereof to provide a ceramic honeycomb structure, a ceramic honeycomb catalyst carrier, and a ceramic honeycomb catalytic converter using these, capable of preventing damage to the ceramic honeycomb catalyst carrier in a sure manner by means of preventing cracks at the perimeter of the ceramic honeycomb catalyst carrier.

[0006] According to a first aspect of the present invention, there is provided a ceramic honeycomb structure comprising ; a ceramic honeycomb body prior to carrying a catalyst, and a material adhered to the entire outer side of an outer wall of the ceramic honeycomb body, the material having a thermal expansion co-efficient approximately the same as that of the catalyst.

[0007] Here, the material which has a thermal expansion co-efficient approximately the same as that of the catalyst is preferably waterproof.

[0008] Also, according to a second aspect of the present invention, there is provided a ceramic honeycomb catalyst carrier comprising; a ceramic honeycomb catalyst carrier, and a material adhered to the entire outer side of an outer wall of the ceramic honeycomb catalyst carrier, the material having a thermal expansion co-efficient approximately the same as that of the catalyst.

[0009] The primary constituent of the material which has a thermal expansion co-efficient approximately the same as that of the catalyst is preferably one of the following; γ-Al_2O_3, α-Al_2O_3, and mullite. Also, the partition thickness of the ceramic honeycomb structure is preferably 0.12 mm or thinner.

[0010] Further, according to a third aspect of the present invention, there is provided a ceramic honeycomb catalyst converter comprising the above-described ceramic honeycomb structure fixed within a metal case by means of a holding material, and subsequently caused to carry a catalyst.

[0011] Still further, according to a fourth aspect of the present invention, there is provided a ceramic honeycomb catalyst converter comprising the above-described ceramic honeycomb catalyst carrier fixed within a metal case by means of a holding material.

[0012] Now, the holding material here is preferably a non-intumescent ceramic fiber mat.

BRIEF DESCRIPTION OF THE DRAWINGS

[0013]

Fig. 1A is a schematic perspective view of an example of the ceramic honeycomb structure according to the present invention;
Fig. 1B is a frontal view of that shown in Fig. 1A;
Fig. 2A is a schematic perspective view of an example of the ceramic honeycomb catalyst carrier according to the present invention;
Fig. 2B is a frontal view of that shown in Fig. 1A;
Fig. 3 is a schematic explanatory diagram of an example of a ceramic honeycomb catalytic converter;
Fig. 4A is a drawing illustrating the results of crack observation of a ceramic honeycomb catalyst carrier according to the first through fourth embodiments of the present invention following endurance testing;
Fig. 4B illustrates the results of the same with a first comparative example thereof; and
Fig. 4C illustrates the results of the same with a second comparative example.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0014] The ceramic honeycomb structure according to the present invention is formed by adhering a material 50 which has a thermal expansion co-efficient approximately the same as that of a catalyst to the entire outer side of the outer wall of a ceramic honeycomb structure 10 before carrying the catalyst, as shown in Figs. 1A and 2B.
[0015] Also, the ceramic honeycomb catalyst carrier according to the present invention is formed by adhering a material 50 which has a thermal expansion co-efficient approximately the same as that of the catalyst to the entire outer side of the outer wall of a ceramic honeycomb catalyst carrier 25, as shown in Figs. 2A and 2B.
[0016] The adhered thickness t of the material 50 which has a thermal expansion co-efficient approximately the same as that of the catalyst may be approximately the same thickness as the catalyst carried on partitions within the ceramic honeycomb catalyst carrier, but more preferably is determined such that the thermal expansion co-efficient be approximately the same for the outer side and inner side of the outer wall of the ceramic honeycomb catalyst carrier.
[0017] Specifically, in the case of causing a ceramic honeycomb structure manufactured of cordierite (partition wall thickness of 0.06 mm, and 140 cells/cm^2) to carry a Pd catalyst (amount of precious metal, 150 g/ft^3, and wash coat amount, 200 g/liter), the adhering is preferably made to the entire outer side of the ceramic honeycomb structure at a thickness of 10 to 50 μm.
[0018] From the above, the thermal expansion difference between the outer side and inner side of the outer wall of the ceramic honeycomb catalyst carrier can be solved, by using the ceramic honeycomb structure or the ceramic honeycomb catalyst carrier according to the present invention.
[0019] Thus, cracks occurring at the perimeter of the ceramic honeycomb catalyst carrier in actual use can be prevented, so damage to the ceramic honeycomb catalyst carrier can be prevented in a sure manner.
[0020] Also, in the event that the ceramic honeycomb structure according to the present invention is to be used as a canning structure (a structure wherein the ceramic honeycomb structure before holding the catalyst is fixed by a holding material compressed within the metal case beforehand), the material which has a thermal expansion co-efficient approximately the same as that of the catalyst is preferably waterproof.
[0021] This is to enable inhibiting clogging of the outermost cells of the ceramic honeycomb structure with the catalyst by the holding material absorbing water via the partitions at the perimeter of the ceramic honeycomb structure in the catalyst carrying process.
[0022] As for the material which has a thermal expansion co-efficient approximately the same as that of the catalyst used with the present invention, preferably used is such which has one of γ-Al_2O_3, α-Al_2O_3, or mullite as the principal constituent thereof, which have thermal expansion co-efficients equal to or close to γ-Al_2O_3 which is the principal constituent of the wash coat (used for forming an activated alumina layer film on the interior of the ceramic honeycomb structure).
[0023] Also, waterproofing the material which has a thermal expansion co-efficient approximately the same as that of the catalyst can be realized by adding an appropriate amount of water-soluble acrylic resin, polyethylene resin, etc.
[0024] The present invention is more effective the thinner the partition thickness of the ceramic honeycomb structure is, and is preferably applied to such of 0.12 mm or thinner. This is because the thinner the partition thickness is, the easier cracks occur at the perimeter of the ceramic honeycomb structure.
[0025] Next, the ceramic honeycomb catalytic converter according to the present invention is formed by fixing the above ceramic honeycomb structure within a metal case by means of a holding material, and subsequently causing this to carry a catalyst.
[0026] Also, the ceramic honeycomb catalytic converter according to the present invention is formed by fixing the

above ceramic honeycomb catalyst carrier within a metal case by means of a holding material.

[0027] Now, with the ceramic honeycomb catalytic converter according to the present invention, the holding material used is preferably a non-intumescent ceramic fiber mat. This is because the holding pressure only 1/3 to 1/10 as compared to conventional expanding holding material, and cracks easily occur at the perimeter of the ceramic honeycomb structure.

[0028] Now, the present invention will be described in further detail with reference to embodiments, by the present invention is by no means restricted to these embodiments.

First Embodiment through Third Embodiment

[0029] Ceramic honeycomb structures manufactured of cordierite, with a diameter of 106 mm, length of 114 mm, partition wall thickness of 0.06 mm, 140 cells/cm^2, and a thermal expansion co-efficient of 0.6×10^{-6}/°C, were prepared for each.

[0030] An activated alumina layer film was formed on the interior of the ceramic honeycomb structures with a wash coat amount of 200 g/liter, following which a Pd catalyst (amount of precious metal, 150 g/ft^3) was carried thereby.

[0031] Next, the entire outer side of the outer walls of the ceramic honeycomb structures were respectively coated with materials having the substance shown in Table 1 as the primary constituent thereof, to the thickness shown in Table 1, thereby forming ceramic honeycomb catalyst carriers according to the present invention (First through Third Embodiments).

Fourth Embodiment

[0032] A ceramic honeycomb structure manufactured of cordierite, with a diameter of 106 mm, length of 114 mm, partition wall thickness of 0.06 mm, 140 cells/cm^2, and a thermal expansion co-efficient of 0.6×10^{-6}/°C, was subjected to coating on the entire outer side of the outer wall with the material having the substance shown in Table 1 as the primary constituent thereof, to the thickness shown in Table 1, thereby forming a ceramic honeycomb structure according to the present invention.

[0033] Next, the ceramic honeycomb structure was fixed within the metal case by a holding material (non-intumescent ceramic fiber mat), thus forming a canning structure, and an activated alumina layer film was formed on the interior of the above canning structure with a wash coat amount of 200 g/liter, following which a Pd catalyst (precious metal amount, 150 g/ft^3) was carried, thereby manufacturing a ceramic honeycomb catalytic converter (Fourth Embodiment).

Table 1

	Material with thermal expansion co-efficient approximately the same as that of catalyst		Average thickness of application (μm)
	Primary constituent	Thermal expansion co-efficient (10^{-6}/°C)	
First Embodiment	γ-Al_2O_3	7.1	25
Second Embodiment	α-Al_2O_3	8.0	20
Third Embodiment	Mullite	5.3	30
Fourth Embodiment	γ-Al_2O_3 + water-soluble acrylic resin	7.1	25

* Catalyst (Pd-Al_2O_3): 7.3×10^{-6}/°C

First Comparative Example

[0034] A ceramic honeycomb structure manufactured of cordierite, with a diameter of 106 mm, length of 114 mm, partition wall thickness of 0.17 mm, 62 cells/cm^2, and a thermal expansion co-efficient of 0.6×10^{-6}/°C, was prepared.

[0035] An activated alumina layer film was formed on the interior of the ceramic honeycomb structures with a wash coat amount of 200 g/liter, following which a Pd catalyst (amount of precious metal, 150 g/ft^3) was carried thereby, thus manufacturing a ceramic honeycomb catalyst carrier (First Comparative Example).

Second Comparative Example

[0036] A ceramic honeycomb structure manufactured of cordierite, with a diameter of 106 mm, length of 114 mm, partition wall thickness of 0.06 mm, 140 cells/cm^2, and a thermal expansion co-efficient of 0.6×10^{-6}/°C, was prepared.
[0037] An activated alumina layer film was formed on the interior of the ceramic honeycomb structures with a wash coat amount of 200 g/liter, following which a Pd catalyst (amount of precious metal, 150 g/ft^3) was carried thereby, thus manufacturing a ceramic honeycomb catalyst carrier (Second Comparative Example).
[0038] The ceramic honeycomb catalyst carriers (First through Third Embodiments, and First and Second Comparative Examples) thus manufactured were fixed within metal cases by a holding material (non-intumescent ceramic fiber mat), thus forming a ceramic honeycomb catalytic converter.
[0039] Endurance testing was performed for each of the obtained catalytic converters (First through Fourth Embodiments, and First and Second Comparative Examples), using a engine dynamo meter. The endurance testing was performed for a total of 500 cycles wherein one cycle consists of 15 minutes heating (maximum temperature 900°C) and 15 minutes cooling (minimum temperature 120°C).
[0040] Following the endurance testing, the ceramic honeycomb catalyst carriers were removed from the metal cases, and cracks in the ceramic honeycomb catalyst carriers were observed using a stereoscope. The results thereof are shown in Fig. 4.

(Examination of First through Fourth Embodiments, and First and Second Comparative Examples)

[0041] From the results shown in Fig. 4, regarding the First through Fourth Embodiments, no cracks whatsoever occurring at the perimeter of the ceramic honeycomb catalyst carrier 28 at the time of actual use could be found, due to application of the material 50 which has a thermal expansion co-efficient approximately the same as that of the catalyst to the entire outer side of the outer wall of the ceramic honeycomb catalyst carrier 25.
[0042] On the other hand, with the First Comparative Example, three cracks were observed at the perimeter of the ceramic honeycomb catalyst carrier 25a, though small. This is because the thermal expansion difference between the inner side of the perimeter which carries the catalyst and the outer side of the perimeter which does not carry the catalyst becomes great.
[0043] Further, with the Second Comparative Example which is a thin wall type, many web-like cracks were observed at the perimeter of the ceramic honeycomb catalyst carrier 25b. Moreover, it was found that part of the cracks had advanced around 20 mm into the interior of the ceramic honeycomb catalyst carrier 25b.
[0044] Thus, the ceramic honeycomb structure, ceramic honeycomb catalyst carrier, and ceramic honeycomb catalytic converter using these according to the present invention is capable of preventing cracks at the perimeter of the ceramic honeycomb catalyst carrier in actual use, and thus is capable of preventing damage to the ceramic honeycomb catalyst carrier in a sure manner.

Claims

1. A ceramic honeycomb structure comprising ;

   a ceramic honeycomb body prior to carrying a catalyst, and
   a material adhered to the entire outer side of an outer wall of said ceramic honeycomb body, said material having a thermal expansion co-efficient approximately the same as that of said catalyst.

2. A ceramic honeycomb structure according to Claim 1, wherein said material having a thermal expansion co-efficient approximately the same as that of the catalyst includes one selected from the group consisting of γ-Al_2O_3, α-Al_2O_3, and mullite, as the primary constituent.

3. A ceramic honeycomb structure according to Claim 1 or 2, wherein said material having a thermal expansion co-efficient approximately the same as that of the catalyst is waterproof.

4. A ceramic honeycomb structure according to any of the Claims 1 through 3, wherein the partition thickness of said ceramic honeycomb structure is 0.12 mm or thinner.

5. A ceramic honeycomb catalyst carrier comprising;

   a ceramic honeycomb catalyst carrier, and
   a material adhered to the entire outer side of an outer wall of said ceramic honeycomb catalyst carrier, said

material having a thermal expansion co-efficeint approximately the same as that of said catalyst.

6. A ceramic honeycomb catalyst carrier according to Claim 5, wherein said material having a thermal expansion co-efficient approximately the same as that of the catalyst includes one selected from the group consisting of γ-Al_2O_3, α-Al_2O_3, and mullite, as the primary constituent.

7. A ceramic honeycomb catalyst carrier according to Claim 5 or 6, wherein the partition thickness of said ceramic honeycomb catalyst carrier is 0.12 mm or thinner.

8. A ceramic honeycomb catalytic converter comprising;

   a ceramic honeycomb structure comprising,
   a ceramic honeycomb body prior to carrying a catalyst, and
   a material adhered to the entire outer side of an outer wall of said ceramic honeycomb body, said material having a thermal expansion co-efficient approximately the same as that of said catalyst, and
   a metal case,
   wherein said ceramic honeycomb structure is fixed within the metal case by means of a holding material, and subsequently caused to carry said catalyst.

9. A ceramic honeycomb catalytic converter according to Claim 8, wherein said holding material is a non-intumescent ceramic fiber mat.

10. A ceramic honeycomb catalytic converter comprising;

   a ceramic honeycomb catalyst carrier comprising,

      a ceramic honeycomb catalyst carrier, and
      a material adhered to the entire outer side of an outer wall of said ceramic honeycomb catalyst carrier, said material having a thermal expansion co-efficient approximately the same as that of a catalyst, and

   a metal case,
   wherein said ceramic honeycomb catalyst carrier is fixed within the metal case by means of a holding material.

11. A ceramic honeycomb catalytic converter according to Claim 10, wherein said holding material is a non-intumescent ceramic fiber mat.

FIG. 1(A)

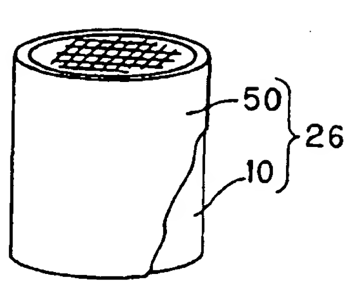


FIG. 1(B)

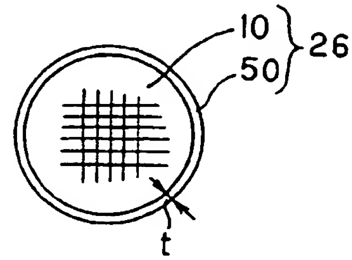


FIG. 2(A)

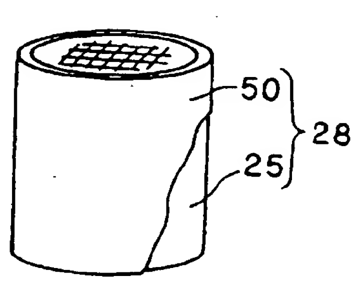


FIG. 2(B)

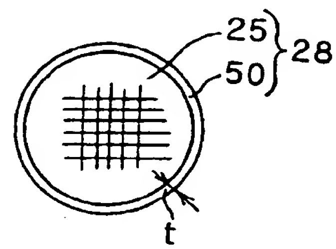


FIG. 3

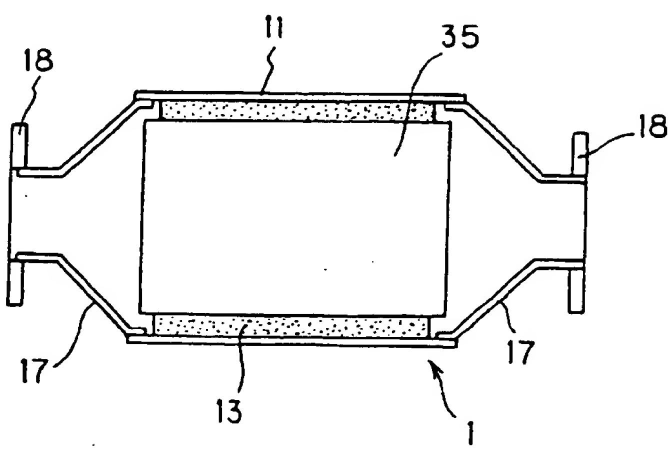


FIG.4(A)

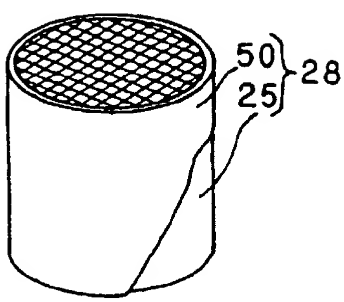


FIG.4(B)

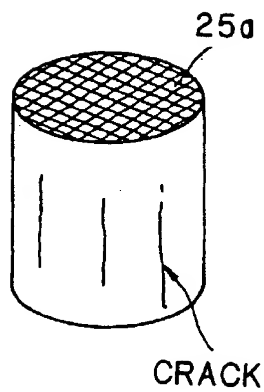


FIG.4(C)

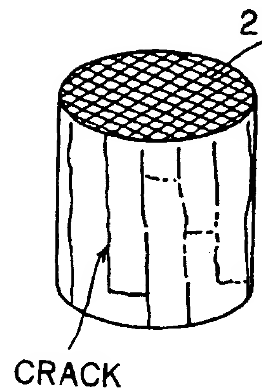


FIG. 1(A)

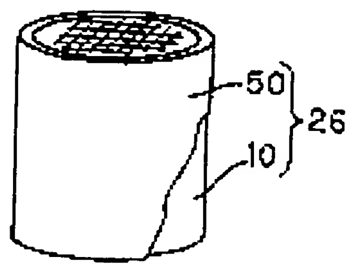


FIG. 1(B)

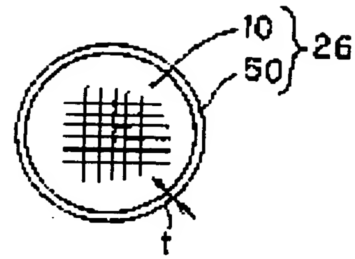


FIG. 2(A)

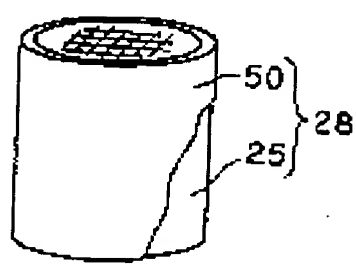


FIG. 2(B)

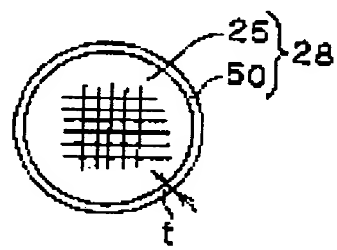


FIG. 3

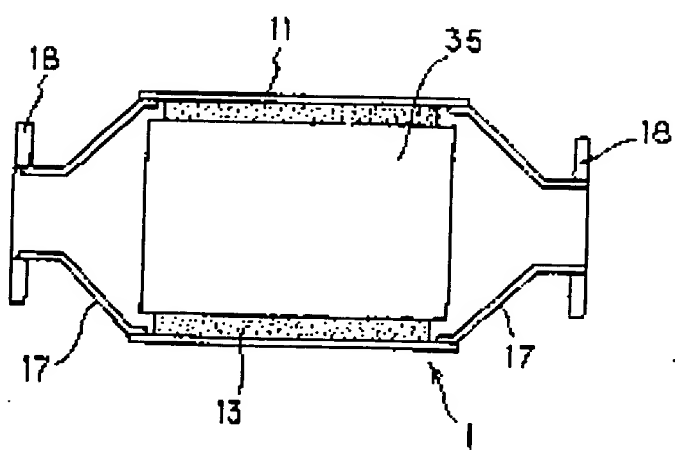


FIG.4(A)

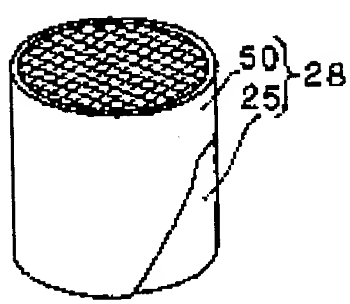


FIG.4(B)

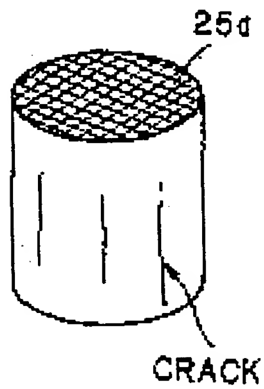


FIG.4(C)